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DETERMINATION OF FLUORINE IN ORGANIC COMPOUNDS

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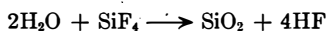
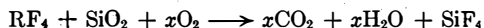
Microcombustion Method

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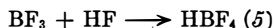
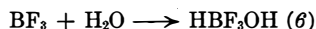
A reliable and widely applicable means of determining fluorine in organic compounds has long been needed. Increased interest in this field of research in recent years has intensified the need. Fluorine in organic combinations may be determined by combustion at 900° C. in a quartz tube with a platinum catalyst, followed by an acid-base titration of the combustion products. Certain necessary precautions and known limitations are discussed in some detail. Milligram samples suffice, and the accuracy of the method is about that usually associated with the other halogen determinations. Use of this method has facilitated the work upon organic fluorine compounds in this laboratory and it should prove to be equally valuable to others.

MANY methods and variations of them have been proposed for the determination of fluorine in organic substances (4, 7-9, 11, 12, 14-16, 20, 23), but no method has been found generally applicable to a wide variety of combinations, particularly those involving the presence of trifluoromethyl groupings, other halogens, sulfur, and compounds of little or no hydrogen content.

The determination of fluorine essentially involves two steps: release of the fluorine, and assay of the fluorine so released. In this laboratory combustion with oxygen in a fused quartz or Vycor glass No. 7900 (96% silica) tube was considered the most promising method for the former and an acid-base titration the most direct for the latter. Furthermore, such a procedure should allow the use of standard equipment commonly available. Theoretically, the reactions may be written as follows:



However, in attempting to apply the above equations to the determination of fluorine in pure organic compounds, consistently low results were obtained. A critical consideration of possible combustion products led to the conclusion that boron, a constituent of some combustion tubes and receiving vessels, could be appearing in these products as a boron-fluorine combination which was not titratable with sodium hydroxide under these conditions. If this boron-fluorine combination is assumed to be boron trifluoride, the following equations may represent the reactions involved:

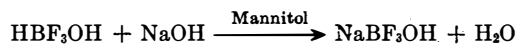


Further hydrolysis has been shown to be very slow under titration conditions (10, 24), and therefore may be disregarded.

In view of the above equations, it appeared that the troublesome end product of boron, which was not titrated directly with sodium hydroxide, might be monohydroxyfluoboric acid (HBF_3OH). This also might explain previous observations concerning the possible cause of low fluorine analyses when boron was present (19). Evidence of the existence of this monohydroxyfluoboric acid has been established by x-ray studies (1) and by the preparation of alkali metal salts (13), but there is some question as to whether it can be titrated directly with alkali (2, 22).

In practice it was found that if the products of combustion were swept into water, warmed to drive out carbon dioxide, and immediately titrated to a phenolphthalein end point with 0.01 *N* sodium hydroxide, there remained a small increment which in turn could be titrated after the addition of mannitol. The addition of polyhydroxy compounds such as mannitol, glycerol, or invert sugars to boric acid to allow direct titration with alkali is a common practice. The author observed also that if the mannitol increment was multiplied by three and added to the initial titration, values very close to theoretical were obtained. This supports the theory of the presence of monohydroxyfluoboric acid, in which the ratio of fluorine to acidic hydrogen is 3 to 1.

The equation for the titration of the mannitol increment may be represented as follows:



DESCRIPTION OF METHOD

Equipment (see Figure 1). The equipment listed is advised where a permanent setup is desired. For occasional determinations an ordinary halogen combustion tube (3, 18) according to ACS specifications but made of fused quartz with borosilicate

glass beads or spiral in the receiver section and any furnace capable of 900° C. will suffice.

Furnace capable of maintaining 900° C., B.

Auxiliary furnace which will accommodate the $\frac{5}{16}$ 10/30 junctions of the combustion tube and the receiver and maintain 350° C., C.

Microcombustion tube, fused quartz, ACS specifications (3) but with a $\frac{5}{16}$ 10/30 male joint formed on one end, D.

Grote-type borosilicate glass receiver (21) with $\frac{5}{16}$ 10/30 standard joint, E, and spray trap, F.

Buret, reservoir type, 5-ml. capacity, at least 0.05-ml. graduations. (The inside of the reservoir and the immersed portion of the buret should be paraffin-coated unless the glass is boron-free.)

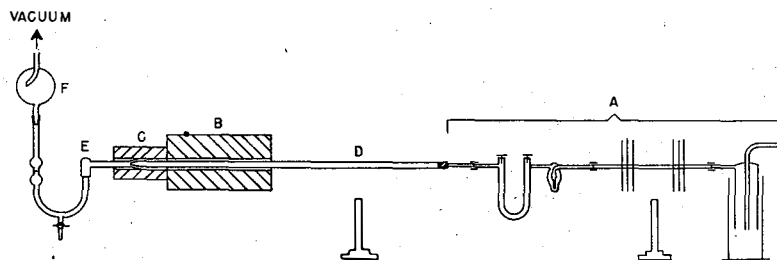


Figure 1. Combustion Train

Reagents. Mannitol, reagent grade.

Phenolphthalein solution, 1% in ethyl alcohol.

Sodium hydroxide, 0.01 N, carbonate- (17) and boron-free.

Platinum, for contact catalyst.

Silver, ribbon or gauze.

PROCEDURE

The customary oxygen purification train and pressure regulator, A, are used. The furnace section, B, of the combustion tube, D, is filled with platinum stars, gauze, or foil freshly etched with aqua regia. Silver ribbon plugs or gauze rolls are placed at the entrance and exit of this furnace section, the latter plug extending well into the auxiliary furnace section, C.

With B at 900° C. and C at 350° C. the Grote-type receiver, E, F, properly filled with distilled water (21) is connected to the combustion tube. The vacuum and oxygen flow are adjusted to allow about one surge per second through the receiver U-tube with an oxygen pressure of about 5 to 7 inches (12.5 to 17.5 cm.) of 50% sulfuric acid. This provides a rate of flow of about 60 to 70 cc. of oxygen per minute (21). A high oxygen ratio is required (20).

Solids are introduced in platinum boats and liquids in the usual capillaries made of heat-resistant glass. A 3- to 5-mg. sample appears to be adequate.

The sample is burned as in any combustion determination, allowing 15 to 20 minutes for the combustion, following which the train is flushed for 10 minutes to assure complete transfer of the combustion products. The contents of the receiver are transferred (21) to a 100-ml. beaker with distilled water, heated to boiling to expel carbon dioxide, and titrated immediately to a phenolphthalein end point with carbonate-free, boron-free 0.01 N sodium hydroxide. One more washing of the receiver with freshly boiled distilled water to check completeness of the transfer is advisable at this point. If it is complete, approximately 0.5

gram of mannitol is added and the titration is again carried out to the same end point.

CALCULATIONS

$$\frac{[(\text{Initial increment}) \text{NaOH} + 3(\text{mannitol increment}) \text{NaOH}](N)(\text{mil. eq.})(100)}{\text{Sample weight}} = \% \text{F}$$

Example, $\text{C}_{12}\text{H}_8\text{F}_2$. Theoretical fluorine content = 19.98%

$$\frac{[(6.090 \text{ ml.}) + 3(0.210 \text{ ml.})](0.008265)(19)(100)}{5.277 \text{ mg.}} = 20.00\%$$

Experimental data for representative compounds analyzed are listed in Table I.

INTERFERENCES

Silver ribbon or gauze is added to the combustion tube filling, so that other halogens and sulfur will be selectively removed and will not interfere.

Metals in the sample interfere by the retention of fluorine.

Acids resulting from the combustion of compounds containing nitrogen and phosphorus are not removed and they interfere.

REMARKS

Gelatinous silica is deposited on the walls of the receiver and as the deposit accumulates it becomes difficult to obtain complete transfer of the acid products. This gel may be removed by agitating with water and sea sand.

If the tube filling is allowed to protrude about 2 cm. from the furnace section toward the sample, the tendency for explosion is greatly reduced (21).

Vycor glass No. 7900 (96% silica) contains boron, iron, and alumina, which make combustion tubes formed from it undesirable for this purpose.

Because of difference in thermal expansion, the joint between the receiver and the combustion tube should be retightened after warming and always disconnected before cooling.

The platinum contacts should be re-etched with aqua regia

Table I. Analyses

Compound	Molecular Formula	Carbon		Hydrogen		Fluorine		Other Halogens		
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Total
Fluorobenzoic acid	$\text{C}_7\text{H}_5\text{O}_2\text{F}$	60.00	59.89	3.60	3.45	13.56	13.78 13.35 13.92
Difluorobiphenyl	$\text{C}_{12}\text{H}_8\text{F}_2$	75.78	75.93	4.24	4.34	19.98	19.85 19.87 19.98 20.05 20.00
Tetrafluorobiphenyl	$\text{C}_{12}\text{H}_4\text{F}_4$	63.72	63.94	2.67	2.69	33.60	33.30	99.93
Hexafluorobiphenyl	$\text{C}_{12}\text{H}_2\text{F}_6$	54.98	55.06	1.54	1.51	43.49	43.46	100.03
Monofluoroterphenyl	$\text{C}_{18}\text{H}_{12}\text{F}$	87.07	86.95	5.28	5.41	7.65	7.85	100.21
Benzotrifluoride	$\text{C}_7\text{H}_5\text{F}_3$	57.54	57.56	3.45	3.60	39.01	38.73	99.89
Trifluorobenzene	$\text{C}_6\text{H}_3\text{F}_3$	54.56	54.59	2.29	2.19	43.15	42.90	99.68
Tetrafluorobenzene	$\text{C}_6\text{H}_2\text{F}_4$	48.01	48.21	1.35	1.43	50.64	50.43	100.07
Polytetrafluoroethylene (Teflon)	$(\text{C}_2\text{F}_4)_x$	24.02	23.77	0.0	0.0	75.99	76.11	99.88
Dibromodifluorobenzene	$\text{C}_6\text{H}_2\text{F}_2\text{Br}_2$	26.50	26.61	0.74	0.74	13.98	13.48	58.78	58.91	99.74
Fluorochlorobenzene	$\text{C}_6\text{H}_4\text{FCl}$	55.20	55.45	3.09	3.22	14.55	14.85	27.16	26.95	100.47
Difluorochlorobenzene	$\text{C}_6\text{H}_3\text{F}_2\text{Cl}$	48.51	48.76	2.03	1.98	25.58	25.72 25.88
Difluorodichlorobenzene	$\text{C}_6\text{H}_2\text{F}_2\text{Cl}_2$	39.38	39.37	1.10	1.24	20.77	21.17 20.82
1-Chloro-2,5-difluorobenzotrifluoride	$\text{C}_7\text{H}_2\text{F}_5\text{Cl}$	38.82	38.58	0.93	1.11	43.87	43.99	16.38	16.59	100.27
Trifluoriodobenzene	$\text{C}_6\text{H}_3\text{FI}$	27.93	28.14	0.78	0.85	22.10	21.97
Difluorobromobenzene	$\text{C}_6\text{H}_4\text{F}_2\text{Br}$	37.34	37.43	1.56	1.62	19.69	20.19	41.41	41.06	100.3
Polytrifluorochloroethylene (Kel-F)	$(\text{C}_2\text{F}_3\text{Cl})_x$	20.62	20.57	0.0	0.47	48.94	48.42
Benzenesulfonyl fluoride	$\text{C}_6\text{H}_5\text{SO}_2\text{F}$	44.99	45.02	3.13	2.92	11.86	12.03

each time that they are handled. More frequent treatment appears unnecessary.

SUMMARY

Fluorine in organic substances may be determined by combustion at 900° C. with oxygen in a fused quartz combustion tube, followed by an acid-base titration using phenolphthalein as the indicator. A second titration after the addition of mannitol is necessary to account for the fluorine of a boron-fluorine combination. Other halogens and sulfur do not interfere. Nitrogen, phosphorus, and metals do interfere, but no other limitation was encountered and none is anticipated. Milligram samples suffice, and accuracy appears to be about that usually associated with the other halogen determinations. Further work is in progress upon various phases of this study.

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